

Detection of Superoxide Radicals on the Surface of Illuminated TiO₂ Powders by Luminol in Air

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The lifetime and productivity of superoxide radicals on photoirradiated TiO₂ powders was investigated by monitoring chemiluminescence on the addition of luminol solution.

Photocatalytic reactions, based on photoelectrochemical processes at the surface of photoirradiated TiO₂ semiconductor have attracted much interest because of its practical applications to the clean-up of building materials and the mineralization of waste water. Under an aerated condition, superoxide radicals (O₂^{•-}) play an important role in the photocatalytic reactions as well as OH radicals. However, superoxide radicals could not be detected directly by conventional spectroscopic techniques such as optical absorption and electron spin resonance (ESR) spectroscopies under the ambient condition. To detect the active species of very low amounts, we first applied a chemiluminescent probe, luminol, successfully to semiconductor photocatalytic reactions in the aqueous TiO₂ suspension.¹⁾ The amount of the superoxide radical was estimated from the intensity of chemiluminescence on the addition of luminol to TiO₂ powders after the end of the photoirradiation. In the present study, this technique is applied to TiO₂ powders exposed to air. The photocatalytic formation of O₂^{•-} was investigated for various kinds of commercially available TiO₂ powders, which are Degussa P25 (Japan Aerosil), Hombikat UV100 (Sachtleben Chemie), ST-01 (Ishihara Techno), F4 (Showa Titanium), and AMT-100, and AMT-600 (TAYCA), and calcined powders for each TiO₂.

At first by changing irradiation times ranging from 1 to 15 min for some TiO₂ samples, the intensity of chemiluminescence (CL) was observed from 1 s after the end of the irradiation. The irradiation time of 10 min was found to be enough to reach to the steady CL intensities. The CL intensity decayed within few seconds by the reaction with luminol. Next in order to investigate the lifetime of the reactive species, the addition of the luminol solution was delayed from 1 s to 500 s after the end of irradiation. Figure 1 represents the observation of CL for different delay times. By integrating the CL intensity over 20 s for each delay time, the decay profile of the reactive species in the absence of luminol was obtained as shown in Figure 2. The reactive species which induces CL was assigned to O₂^{•-} based on the following evidences; the decay rate is proportional to the concentration of luminol injected, the similar decay was observed with another CL probe specific to O₂^{•-},²⁾ and the decay rate with luminol can be simulated according to the reported parameters.¹⁾

The above results indicated that O₂^{•-} produced on TiO₂ powder have a significantly long life-time (~200 s), comparing with 17 s in aqueous suspension¹⁾ and 50 s at the surface of TiO₂ film³⁾. When the reciprocal value of the CL intensity in Figure 2 is replotted, the linear correlation was obtained, indicating that O₂^{•-} decays by the disproportionation. Among the various properties of TiO₂, only the secondary particle size showed a correlation with the amount of O₂^{•-} produced. This observation is consistent with that for TiO₂ aqueous

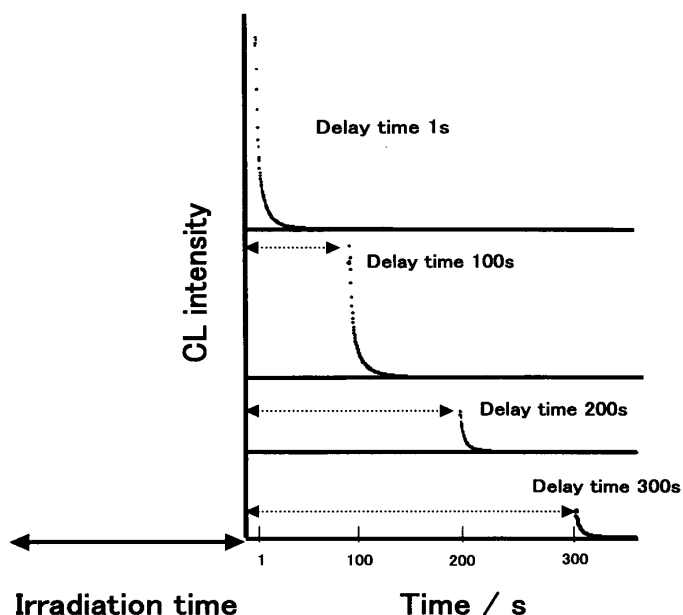


Figure 1. Experimental scheme for chemiluminescence (CL) observation on the addition of luminol solution to TiO₂ powders.

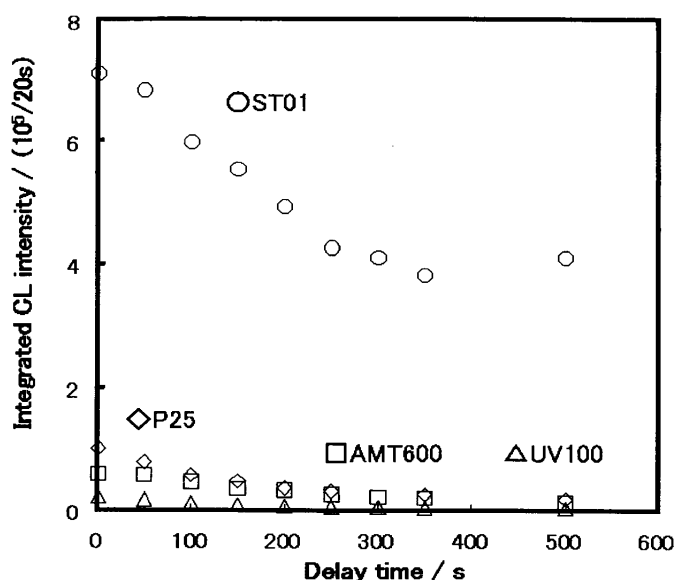


Figure 2. Decay profile of O₂^{•-} was expressed by the integrated CL intensity observed after 10 min irradiation on each TiO₂ powder indicated in the figure.

suspension.¹⁾

The CL intensity decreased for TiO₂ powders calcinated at 573 K, except for ST-01, but increased for those calcinated at 973-1073 K. The decrease is attributable to the release of a surface contaminant that acts as an electron donor while the increase can be explained by the increase in the crystallinity at a higher temperature. Calcination at a higher temperature (1273 K) resulted in the decrease of O₂^{•-} formation again, probably because of the decrease of the anatase content of the samples.

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